

Preparation, Optimization, and Characterization of PMMA/TiO₂-Saffron Dye Nanocomposites: Structural and Physical Properties

Hussein Obaid Mohammed¹

¹Iraqi Ministry of Education, Babylon,, altaehehssein28@gmail.com, Hilla, Iraq.

*Corresponding author email: altaehehssein28@gmail.com ; mobile:+ 9647810391594

تحضير، تحسين، وتصنيف المترافقات النانوية من- صبغة الزعفران: الخصائص البنوية والفيزيائية

حسين عبيد محمد¹

¹ وزارة التربية العراقية، بابل، altaehehssein28@gmail.com ، حلة، العراق

Accepted:

27/10/2025

Published:

31/12/2025

ABSTRACT

This work presents for the first time the development, optimization and structural characterization of titanium dioxide (TiO₂) nanoparticles reinforced poly(methyl methacrylate) (PMMA) nanocomposite functionalized with natural saffron dye belonging to *Crocus sativus* L. The goal was to create a new class of sustainable hybrid materials with improved multifunctional properties. Here, the composites were prepared by solution casting and dip-coating technique with various loading of TiO₂ (0.2, 0.4, 0.6 g wt. %), and were studied with particular focus on its effects upon morphology, dispersion and interfacial interactions. The structural, chemical dimensions and crystallographic investigation of nanocomposites are carried out by XRD, ATR-FTIR and FESEM with Image J analysis of particles for determining nanoparticle dispersion. Results proved the presence of crystal anatase TiO₂, amorphous PMMA phase, good interface bonding facilitated by saffron dye and homogeneous dispersion with slight agglomeration at higher loadings. The hence obtained findings are indicative of strong interfacial interaction. The average particle sizes show a dramatic decrease from around 45 nm at lower TiO₂ contents to 10 nm, suggesting the natural dispersion of the dye. The addition of TiO₂ enhanced its integrity and structure, saffron dye provided optical function as well as bio-function to this novel class of nanocomposite system for possible: opto-electronic, bio-medical coating and eco-friendly materials development.

Key words: Composite materials, poly(methyl methacrylate) (PMMA), natural saffron (*Crocus sativus* L.) dye, titanium dioxide (TiO₂) nanoparticles.



INTRODUCTION

Composite materials represent a sophisticated type of engineering system in which two or more components of distinct nature are assembled to realize performance properties exceeding those of the original elements [1,2]. The reinforcement has historically been supplied by constituents such as fibers, whiskers or particulates in metals, ceramics or polymers and mechanical, thermal and chemical behavior to promote these were improved for an array of applications including aerospace, structural materials, biomedical devices and energy technologies [3,4]. The evolution from fiber-reinforced composites to more complex multifunctional nanostructured systems is in a line with current emerging trends towards lightweight and high-performance materials in modern engineering [2].

From the various matrix polymers which are commonly used, we have paid particular attention to poly(methyl methacrylate) (PMMA), because PMMA is optically transparent and relatively inexpensive with good mechanical properties and chemical resistance [5,6]. Its inherent features of high light transmission, fine environmental stability and excellent resistance to hydrolytic degradation make it a promising alternative for glass in various optical, electronic and biomedical applications [7,8]. However, pristine PMMA exhibits intrinsically poor toughness as well as a low resistance to UV irradiation and thermal stress which limit its application in high-grade toughening and durable uses [8–11].

In response to these challenges, the use of nanoscale fillers has become a revolutionary approach. Polymer nanocomposites as a new class of material have the nanoparticles with very high surface areas and novel interfacial activity, which lead to significant improvements in stiffness, strength, fracture toughness, and dimensional stability [12]. Metal oxides (i.e., TiO₂ [13,14], SiO₂, ZnO[15]), and carbon-based nanofillers have been extensively studied to improve structural, electrical, optical properties [16,17]. The effectiveness of such reinforcements is, however, highly sensitive to the realization of homogeneous dispersion in the matrix and control over interfacial interactions that define stress transfer and property evolution [18].

TiO₂ nanoparticles, in particular, have attracted a lot of attention because of their multiple benefits such as high refractive index; photoactivity all through the UV spectrum and UV absorption, for instance [19]. Their introduction into PMMA matrices has been presented to enhance thermal stability, rising of T_g, continue and optical parameters as well [20]. However, TiO₂ nanoparticles are highly polar and have high surface energy; therefore, they can agglomerate at a higher loading level to reduce their reinforcement effect. This difficulty has spurred the efforts to modify surface particles in order to minimize particle-particle contacts and promote homogeneous distribution within the organic matrix. With such methods, PMMA/TiO₂ nanocomposites render better performance in structural and functional applications including optical, electronic and biomedical fields [21].

The use of natural dyes for the preparation of chromatic functional polymers, which are being designed with specific optical, biological and therapeutic properties for potential technological and biomedical applications is a promising frontier in macromolecular technology [22]. Of these natural pigments, saffron (*Crocus sativus* L.) has gained interest as a coloring agent not only in the



traditional sense, but also with its various pharmacological, cosmetic and nutraceutical properties [23]. Its bioactivity is mainly due to its rich content in crocin and safranal, which mediate its vivid appearance, antioxidant activity and antimicrobial action. Crocin is a water-soluble carotenoid glycoside) and responsible for its neuroprotective, anti-inflammatory and antidepressant properties, while safranal (a volatile monoterpane aldehyde) is responsible for the aroma as well as the antibacterial action. The synergism of these ingredients would promote antiseptic, antimicrobial and soluble, volatile nature of saffron dyes via ionic interaction with SA providing multi-effective therapeutic advantages [24]. The extracts of saffron have been used as sedatives, antispasmodics, expectorants and aphrodisiac in traditional medicine, and their therapeutic effects against the management of neurological, gastrointestinal and reproductive ailments have already been proved. These multipurpose properties further broaden the function of saffronoid dyes beyond mere colorants, as they can be used biofunctional chromophores with outstanding potential in biomedicine, pharmaceuticals and agro-food applications. It should be noted that, in contrast to artificial dyes like the synthetic Safranin O dye with environmental and toxicological issues, saffrons dyes present the benefits of biocompatibility, biodegradability and sustainability, making them as an excellent candidate for incorporation into organic–inorganic hybrid nanocomposites for future optical, biomedical and environmental applications.

Significant advancements have been made in PMMA/TiO₂ composites and dye-modified polymer complex systems that have been shown in earlier studies; this notwithstanding, significant deficiencies exist. Early work by Caris et al. [25] emphasized the potential of surface-modified TiO₂ to promote strong polymer–particle coupling in emulsion polymerization but was restricted to coatings/paints instead of multifunctional nanocomposites. Chen [26] and Agarwal [27] studied the adding of TiO₂ to PMMA, it results in better thermal stability and mechanical properties but they only focuses on polymerization or phase transition not optical or biological functionalities. Kadhem [28] broadened the range for thin-film systems composite to exhibit a variable optical band gap due to the incorporation of TiO₂, although bioactive/natural dyes were not included to contribute with the multifunctional character. Similarly, Darweesh et al. [29] studied Safranin doped PMMA films and found changes to the optical transitions, however no inorganic fillers were included for mechanical or structural reinforcement. More recently, Hameed et al. [30] added saffron dye into PMMA/nano-HA composites and showed the antibacterial property along with crystallinity enhancement; however, they were concentrating more on HA, and TiO₂ in partnership with natural dyes was not explored. Overall, these data highlight an obvious research question: although thermal, mechanical and optical upgrading of PMMA/TiO nanocomposites have been studied as well as biological activity effect of natural dyes like saffron dye is produced in the body; however, scarce enquiries are available regarding the combination with TiO₂ particles and natural dyes (e.g. saffron) within PMMA matrix. Such hybrid systems could benefit from structural reinforcement of TiO₂ and optical as well as functional properties of saffron dye along with the flexibility of PMMA, further contributing to shape solution toward the development of sustainable multi-functional nanocomposites having combined structural, optical and bioactive properties.

The main objective of this study is to synthesize and characterize poly(methyl methacrylate) (PMMA)-nanocomposites reinforced with titanium dioxide (TiO_2) nanoparticles and functionalized by saffron (*Crocus sativus L.*) dye for the development of green versatile materials designed with improved structural, optical and bioactivity. Although TiO_2 has been used previously as a reinforcing component to improve the thermal and mechanical stability of PMMA, and natural dyes such as saffron have been incorporated for plant-based antimicrobial activity²⁹ and optical properties³⁰ in isolation, there is little by way of reports that document these two components existing synergistically within a single PMMA matrix. The novelty of this work is to fill that gap by developing a hybrid organic–inorganic means, which captures the reinforcing effect of TiO_2 nanoparticles and incorporates the chromophoric (colorant) and biofunctional activities of saffron dye, and takes advantage of the versatility to mix with PMMA as polymer host.

EXPERIMENTAL SECTION

Utilized Materials

Poly(methyl methacrylate) (PMMA) used in pellet form was procured from Shanghai Kaidu Industrial Development Co., Ltd., China. The saffron natural dye was prepared from *Crocus sativus L.* stigmas and extracted by a drying technique according to the procedure described in [31]. The extraction solvent was chloroform (IUPAC name: trichloromethane, $CHCl_3$), a clear colorless volatile and high-density organic liquid having strong smelly odor with wide solvating ability. Chloroform was chosen for its known ability to dissolve both polymeric matrices and organic compounds, enabling homogeneous dye loading into the nanocomposite system.

Preparation of PMMA/ TiO_2 –*Crocus sativus L.* Nanocomposites

Nanocomposite films were prepared by a solution casting and dip coating method. First PMMA-2 g granules were dissolved completely in 63 mL of chloroform in a glass beaker with magnetic stirring at 25 °C for 30 min to have very homogenous solution. From this solution 10 mL was drawn and taken as the base polymer for other composite formulations. The loading of TiO_2 nanoparticles was 0.5–1 wt% into the PMMA solution, as summarized in Table 1. To achieve nanoparticles with uniform distribution and avoid agglomerates, the suspensions were ultrasonicated for 8 min. After achieving nanoparticle suspension, 10 mL of saffron (*Crocus sativus L.*) dye extract solution was mixed with each suspension to form hybrid organic–inorganic nanocomposites. The glass substrates were coated by a dip-coating process, where slides were fixed in a homemade clamp and dipped into the prepared suspensions for 10 min, followed by extraction at 240 mm/min at which both dipping depth of the slide and surface level persisted for 10 s. Coated substrates were kept at the dip-coating device for 30 min to evaporate the solvent and stabilize NPs in polymer matrix.

Table 1. Mixing proportions of the prepared PMMA/TiO₂–Crocus sativus L. nanocomposites.

PMMA (g)	PMMA solution (mL)	PMMA + saffron dye (mL)	TiO ₂ (g)	Final composite composition
2.0	–	–	–	PMMA (control)
1.8	53	63	0.2	PMMA/TiO ₂ –saffron dye
1.6	53	63	0.4	PMMA/TiO ₂ –saffron dye
1.4	53	63	0.6	PMMA/TiO ₂ –saffron dye

Coating process

Dip-coating process is considered one of the easiest, economical methods for thin film synthesis from inorganic, hybrid and nanocomposite materials [32]. The general steps of the process (Figure 2) are as follows: (i) dipping substrate into precursor solution, (ii) extracting substrate with a certain withdrawn speed, and (iii) thin film deposit by solvent evaporation [33]. This process is beneficial, especially for laying down thin films onto substrates of varying morphologies and complex geometry such as perforated or patterned surfaces-and controlling the thickness, morphology and structural characteristics with a high precision. It is carried out by submerging the substrate in the solution to be deposited under controlled temperature and atmospheric conditions, with continuous withdrawal at constant speed. The later process involves a delicate balance between viscous drag and capillary forces in the liquid film, before gelation on solvent evaporation. Important parameters, including the pulling rate, solution viscosity and evaporation process, have a direct effect on microstructure and optical properties of films deposited. Post-deposition heat treatment is often employed to further densify the film, enhance adhesion and tune its physicochemical properties [34].

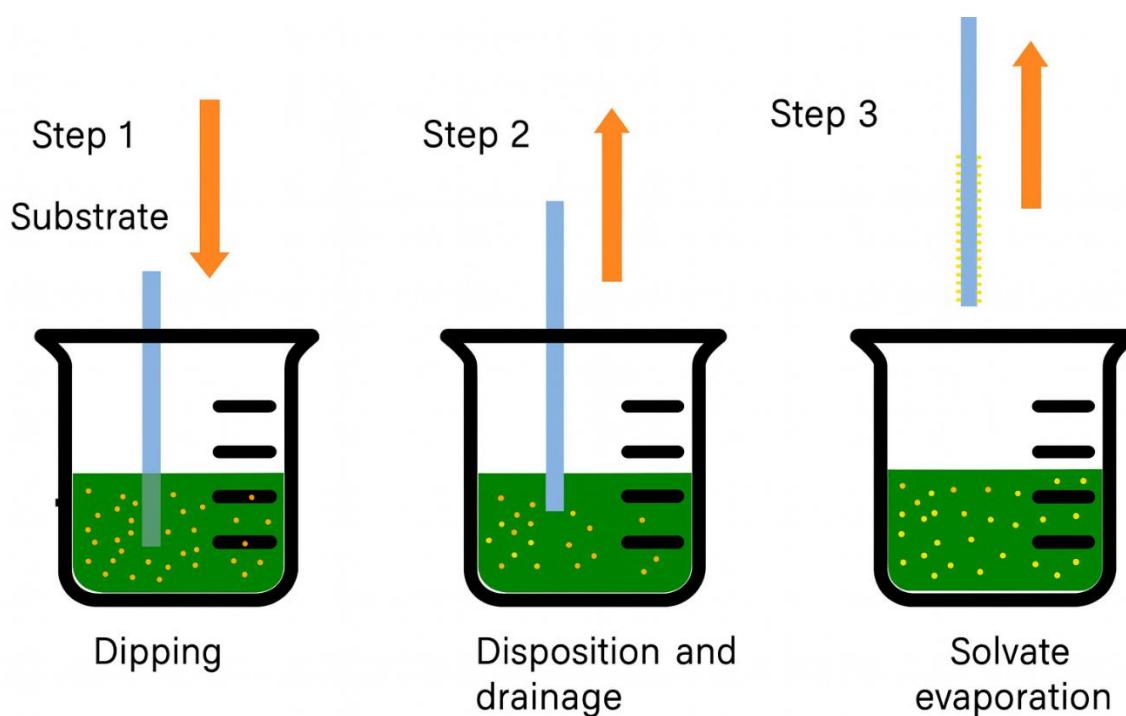


Figure 1. Schematic of the dip-coating process phases.

Characterization Tests

- **XRD Diffraction Analysis**

X-Ray diffraction (XRD) measurements have been performed with a powder diffractometer provided with a double goniometer and Cu K α target radiation ($\lambda = 1.5406 \text{ \AA}$) by setting the voltage at 40 kV and current to 30 mA in Bragg–Brentano θ – 2θ geometry. Samples were scanned over a range of 2θ (10–80°) with a step size of 0.02°, and count rates were optimized for good signal-to-noise values and peak resolution. Sample films or coatings were mounted on low-background silicon holders to reduce scattering contributions and a sample spinner was used for improved averaging during the measurements.

- **FESEM Analysis**

The surface morphologies and microstructures of the fabricated nanocomposites were examined using FESEM. Samples were used as $5 \times 5 \text{ mm}$ sectioned pieces, attached on to aluminum stubs using conductive carbon tape and sputter coated with a thin layer of Au/Pd maintained over the top (at conduction resolution of 1 nm) for surface charge reduction. Images were acquired under high-vacuum conditions at accelerating voltages in the range of 3–10 kV, and working distances from 5 to 8 mm, at several magnifications (from $5\text{k}\times$ up to $100\text{k}\times$) for obtaining information on global morphology as well as on nanoscale features.

- **ATR-FTIR Spectroscopy**

Chemical interactions and functional groups of the nanocomposites were determined by attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy. Spectra were acquired

using a diamond ATR accessory in the wavenumber range of 4000–500 cm^{-1} at a resolution of 4 cm^{-1} , with 32–64 scans co-added per measurement to enhance spectral reliability. To remove CO_2 and H_2O interference in the atmosphere, background spectrums were collected before each sample using same experimental parameters. The films were mounted directly onto the diamond crystal and uniform contact pressure was applied by the integrated pressure arm, to guarantee reproducible evanescent penetration depth.

• **ImageJ Analysis**

Quantitative morphology measurements of the PMMA/TiO₂–saffron dye nanocomposites were carried out by ImageJ (National Institutes of Health, USA). The HRFSEM micrographs of the nanocomposite surfaces were imported into the software where scale bar was adjusted to correspond accurate dimensions. Thresholding and contrast enhancement were applied to the images to be able to differentiate TiO₂ particles from the polymeric surroundings. Particle analysis was subsequently performed to average nanoparticle size, particle counting and spatial distribution within the PMMA matrix. At least ten representative micrographs per composition were examined to reduce chance effects and increase the statistical significance.

RESULTS AND DISCUSSION

X-ray Diffraction

The XRD pattern of the PMMA/nano-TiO₂/saffron dye composite (figure 2) shows well-defined diffraction peaks related to the crystalline anatase phase of TiO₂ dispersed in amorphous PMMA matrix. A strong, high intensity diffraction band observed at $2\theta \approx 25.3^\circ$ was indexed to (101) plane of anatase TiO₂ (JCPDS card no. 21-1272), along with other additional reflection bands at $2\theta \approx 37.8^\circ$ (004), and step planes at approximately 48.0° (200), 54.0° (105), 62.7° (204) and the highest intensity peak occurs at about d-spacing value of approximately 68.8° (116); confirming retention of the crystallinity in form of anatase phase [35]. The sharpness and intensity of these peaks suggest that the TiO₂ nanoparticles maintain their high level of crystallinity in the composite. On the other hand, PMMA adds a wide amorphous peak around $2\theta \approx 13$ – 20° typical for the lack of long-range molecular ordering in polymeric chains. The saffron dye had constituted in an increase of the background scattering, and not introduced other crystalline reflections as is to be expected in case of amorphous organic chromophores. Notably, no reflections were found for rutile or other secondary TiO₂ phases indicating that the anatase phase was maintained throughout processing. This phase stability is desirable because anatase TiO₂ possesses better-performing photocatalytic and optical properties to compare with rutile [35]. The lack of impurity peaks also indicates the high chemical purity of the prepared nanocomposites. These results are consistent with earlier reports that the inclusion of TiO₂ in polymer matrix succeeds to maintain nanoscale crystallinity whereas promoting dispersion and interfacial contacts [36,37].

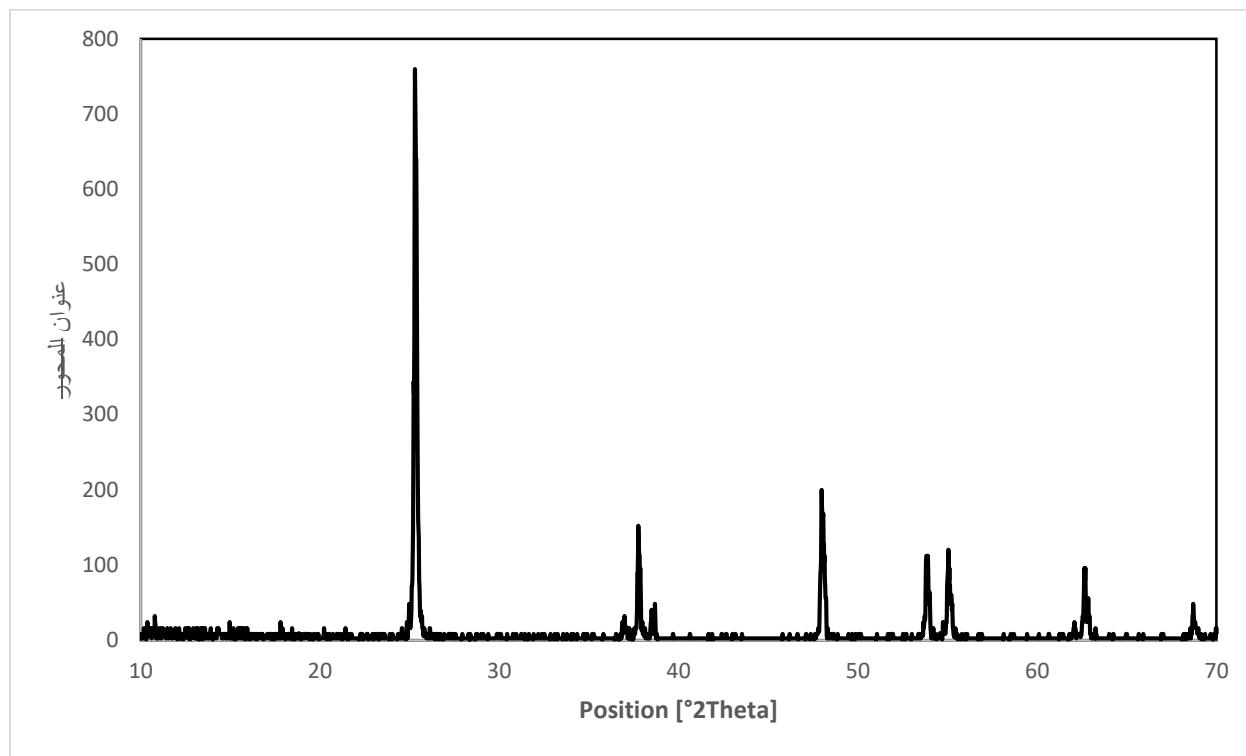


Figure 2. XRD patterns of PMMA/TiO₂–saffron dye nanocomposite (original and smoothed data).

FTIR

Figure 3 presents the FTIR spectra of PMMA/TiO₂–saffron dye nanocomposites with varied TiO₂ contents (0.2, 0.4, and 0.6 wt.%), compared alongside reference spectra of neat PMMA, TiO₂, and saffron dye. The pristine PMMA spectrum exhibits the characteristic ester carbonyl stretching at $\sim 1730\text{ cm}^{-1}$, methyl and methylene C–H stretching modes between 2995–2950 cm^{-1} , and C–O and C–O–C vibrations around 1260 cm^{-1} and 1140–990 cm^{-1} , consistent with established literature [turn0search0]. TiO₂ demonstrates a definitive absorption band below 800 cm^{-1} attributable to Ti–O–Ti lattice vibrations, which becomes increasingly prominent in the composite spectra, confirming the successful integration of the inorganic phase. In the saffron dye, absorption features near 3400–3300 cm^{-1} (O–H stretching) and 1600–1500 cm^{-1} (aromatic C=C/C=N vibrations from crocin and safranal) are discernible. When incorporated into the PMMA matrix, these dye-related bands exhibit reduced intensities and slight peak shifts, strongly implying the formation of hydrogen-bonded or electrostatic interactions between the dye molecules and the polymer chains. Moreover, the observed broadening of the carbonyl band and weakening of the C–O–C peaks in the composite systems suggest interfacial compatibility facilitated by TiO₂ and saffron dye, ensuring improved nanoparticle dispersion and functional synergy. These FTIR observations align with prior reports indicating that spectral shifts and band intensity variations serve as robust evidence of molecular interactions in polymer–nanofiller systems [38].

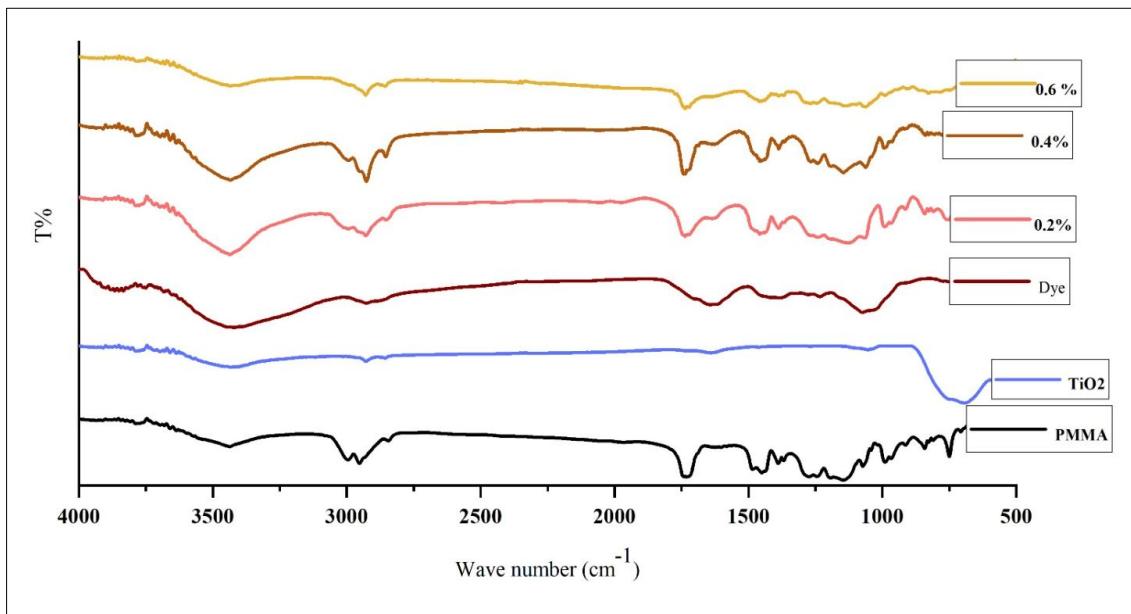


Figure 3. FTIR spectra of PMMA/Nano-TiO₂ composites incorporating saffron dye.

FESEM Analysis

Figure 4 shows FESEM images of poly(methyl methacrylate) (PMMA) at low and high magnifications, evidencing the amorphous and heterogeneous character. Under low magnification, the fracture surface of PMMA looks uneven and coarse due to lacking long range molecular order that is characteristic of an amorphous polymer. At middle magnification, spherical domains are revealed throughout the matrix, which indicates granular polymer morphology and enables favorable anchoring sites to be loaded with nanoparticles. At higher magnification, nanoscale surface texture with particle sizes around ~62 nm is observable in addition to microcavities due to solvent evaporation during the film formation. These morphological features are in agreement with previous reports stating that PMMA films have heterogeneous fracture surfaces and nanoscale structures which could help fillers immobilization, indicating that PMMA film is a suitable host matrix for fabricating hybrid nanocomposites with good structural and optical properties [39–41].

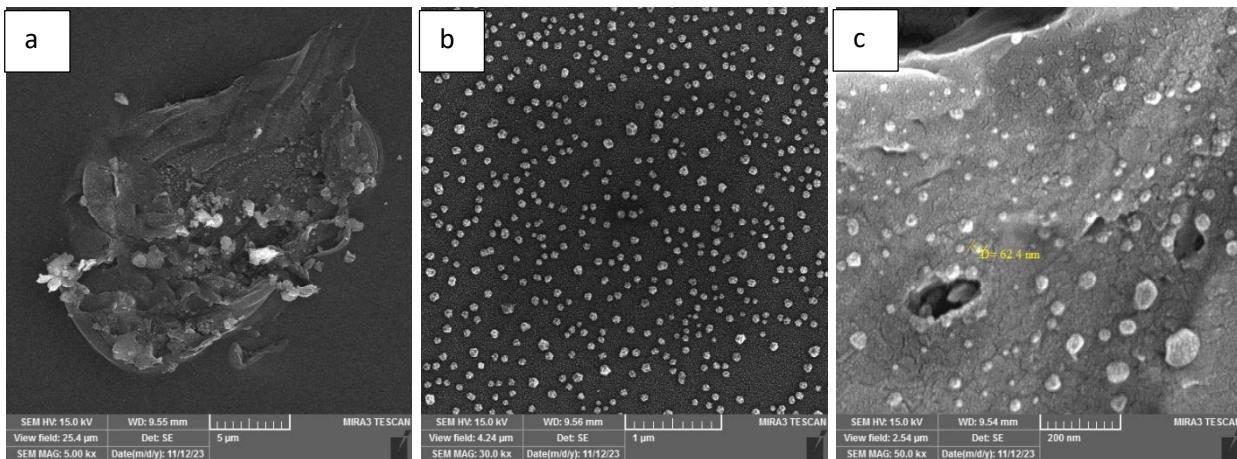


Figure 4. FESEM illustration of PMMA.

Figure 5 presents FESEM images of TiO_2 nanoparticles at different scales revealing their typical agglomerated and nanostructured shape. Under low magnification, the nanoparticles pack into dense porous aggregates with fine nanocrystals owing to their high surface area and interparticle interaction. At such level of magnifications, quasi-spherical nanoparticles with relatively more uniform distributions are distinguishable forming continuous networked structure and pore networks that could induce improved surficial reactivity. At higher magnification, distinct nanoparticles with diameters ranging from ~ 20 to 60 nm are well observed, which is attributed to the anatase phase of TiO_2 prepared from sol-gel and hydrothermal methods. This nanoscale structure, unstable due to agglomeration, has a high specific surface area that is very beneficial for photocatalysis, optical antistatic effect and mechanical reinforcement in composite systems [42,43].

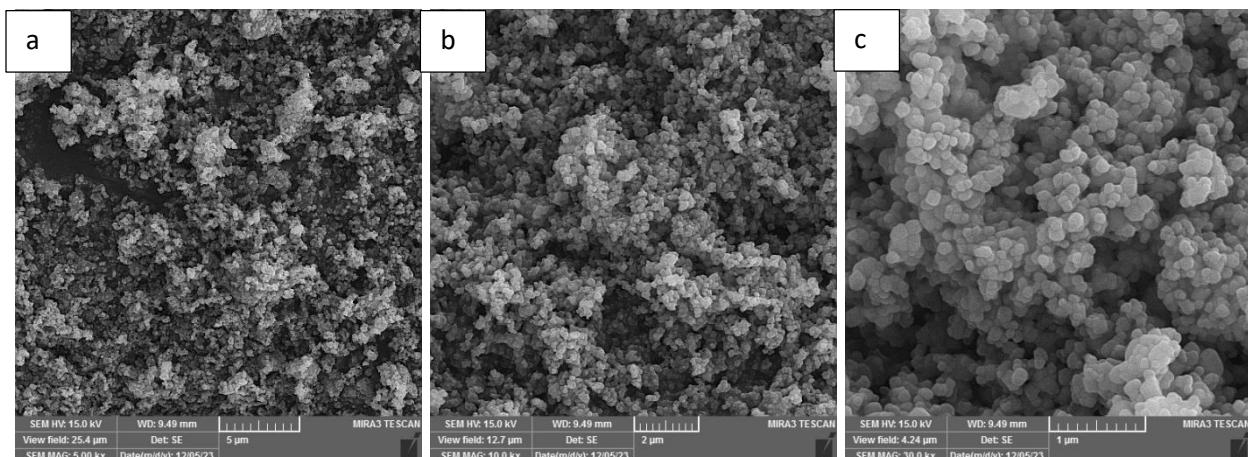


Figure 5. FESEM illustration of TiO_2 .

Figure 6 shows the FESEM images of PMMA/nano-TiO₂–saffron dye nanocomposites at different scale, indicating an effective dispersion of TiO₂ nanoparticles in PMMA and their preservation by the organic dye. Low magnification view of the composite shows a dense granular structure, which is characteristic for uniform dispersion of nanoparticles in the surface of PMMA with particles higher magnifications show quasi-spherical clusters of TiO₂ nanoparticles ranging from ca. 70 to ca. 105 nm in diameter. Cross-sectional images indicate that nanoparticles are embedded in microcavities of the PMMA matrix, which verify strong interfacial adhesion and anchoring effects also strengthened by saffron dye serving as natural organic dispersant. The porous structure in several regions shown here is an evidence for the efficient polymer–nanoparticle dye interactions necessary for enhanced optical absorption, photocatalytic activity and mechanical strength [44,45].

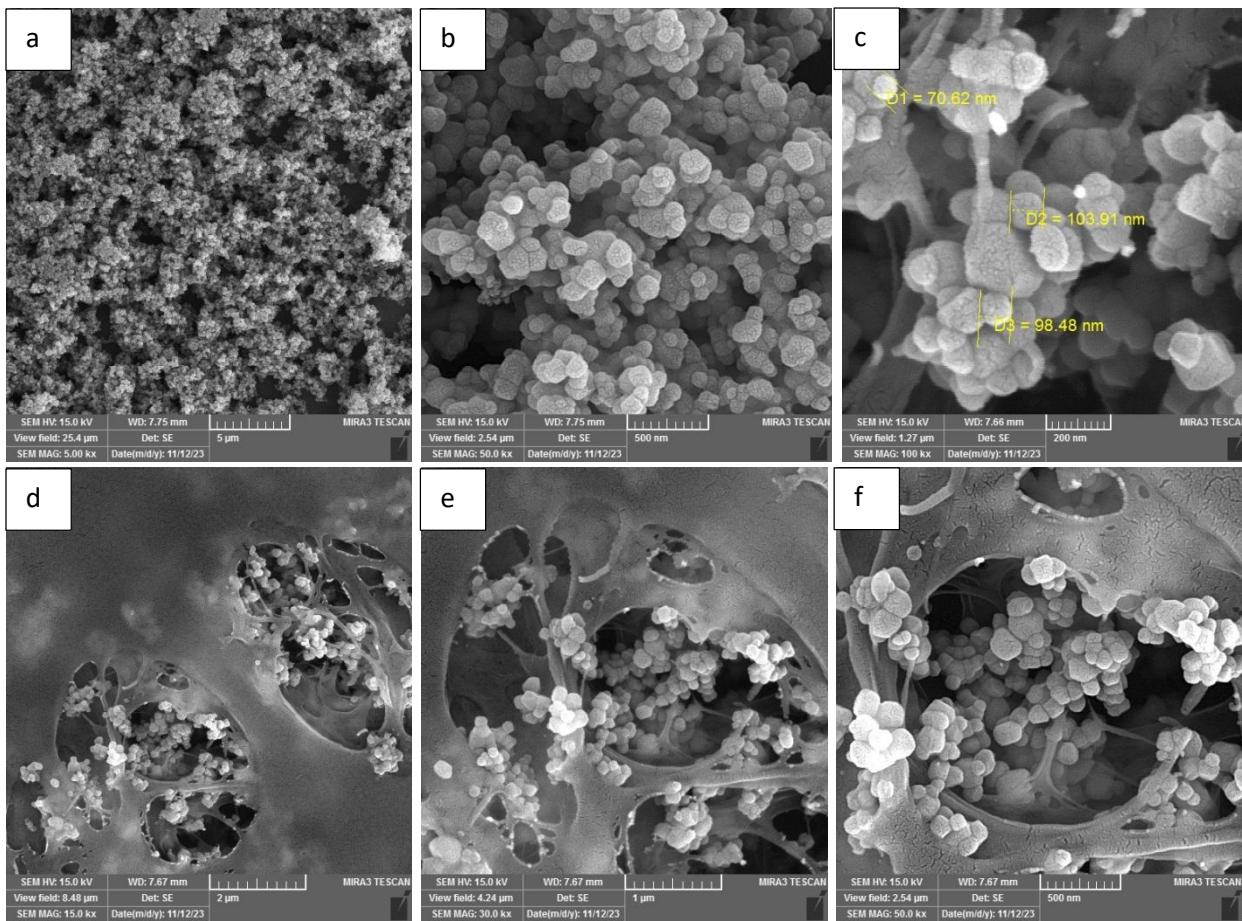


Figure 6. FESEM illustration of (PMMA/Nano-TiO₂+ saffron dye)

ImageJ Analysis

The particle size distribution of nano-TiO₂ in PMMA matrix with saffron dye at two loading (a) PMMA/nano-TiO₂(0.2 g)+ saffron dye(b)PMMA/nano-TiO₂(0.6 g)+saffron dye is shown in Figure 7. In sample (a) the size distribution plotted on the histogram can be considered as relatively wide, varying from ~ 20 to 200 nm, with the peak of most particles at a diameter value around 40–

60 nm and an average size of 44.72 ± 2.07 (nm). A broader distribution in this case indicates that there is partial agglomeration of the TiO_2 nanoparticles at lower loading, which could be caused by van der Waals forces and inadequate steric stabilization within the polymeric medium [46]. In contrast, sample (b) exhibits a marked tendency toward smaller dimensions in the particle size distribution; most of the nanoparticles are gathered below 40 nm and have an average diameter of about 10.54 ± 1.44 nm. The narrow size distribution at high loading of NPs or the larger content at the constant saffron dye is indicative of improvement in saffron dye dispersion and interfacial contact due to increased TiO_2 concentration, which inhibits particles agglomeration [47].

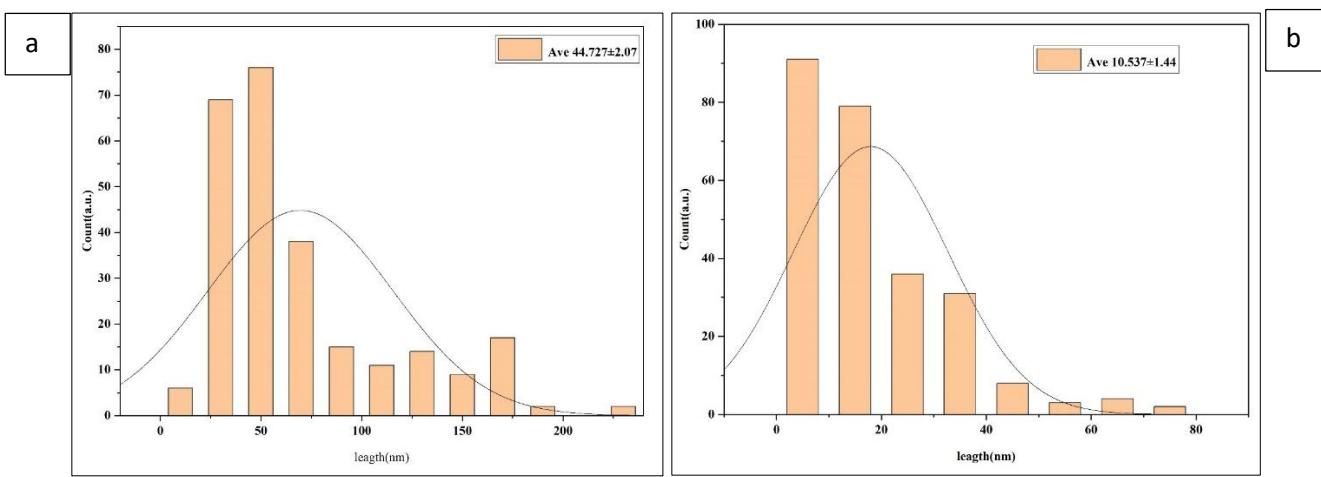


Figure 7. Illustrated the Distributions of the nano- TiO_2 in PMMA (A): modified PMMA (PMMA\Nano- TiO_2 (0.2g) + saffron dye) (B): modified PMMA (PMMA\Nano- TiO_2 (0.6g) + saffron dye)

CONCLUSION

The findings of this study demonstrate that the incorporation of TiO_2 nanoparticles and saffron (*Crocus sativus* L.) dye into the PMMA matrix successfully produced multifunctional nanocomposites with enhanced structural and functional properties.

- The integration of TiO_2 nanoparticles and saffron (*Crocus sativus* L.) dye into the PMMA matrix successfully yielded multifunctional nanocomposites with improved structural and functional properties.
- XRD analysis confirmed the coexistence of amorphous PMMA with crystalline anatase TiO_2 , validating the hybrid structural nature of the composites.
- ATR-FTIR spectroscopy revealed strong interfacial interactions among PMMA chains, TiO_2 nanoparticles, and saffron dye, indicating effective molecular compatibility.
- FESEM imaging coupled with ImageJ analysis demonstrated that higher TiO_2 loading (particularly at 0.6 g) facilitated homogeneous dispersion and reduced agglomeration, with particle sizes decreasing from ~ 45 nm to ~ 10 nm.

- The improved nanoparticle distribution enhanced interfacial bonding and promoted morphological uniformity, contributing to potential reinforcement effects.
- Saffron dye acted as a natural dispersant, stabilizing the nanostructure and imparting additional optical and bioactive functionalities.

Additional research on PMMA/TiO₂–Saffron Dye nanocomposites should assess their biological, adsorption, and photocatalytic properties. Adsorption experiments with dyes like methylene blue or Rhodamine B may determine pollutant removal effectiveness, while antibacterial and antioxidant assays can verify bioactivity. Photocatalytic deterioration under UV or visible light should be tested for self-cleaning and environmental remediation. For biological applications, cytocompatibility and biofilm resistance testing are advised. These studies will establish composites as versatile, eco-friendly, industrially and environmentally relevant materials.

Acknowledgments:

The authors would like to express their sincere gratitude for University of Babylon. Special thanks are extended to the laboratory staff and technical assistants for their valuable support during the experimental work.

Conflict of interests.

The authors decelerates that there is no conflict of interest.

References

- [1] K.K. Chawla, Composite materials: science and engineering, Springer Science & Business Media, 2012.
- [2] S. Simões, High-performance advanced composites in multifunctional material design: State of the art, challenges, and future directions, *Materials* (Basel). 17 (2024) 5997.
- [3] A. Kumar, S. Dixit, S. Singh, S. Sreenivasa, P.S. Bains, R. Sharma, Recent developments in the mechanical properties and recycling of fiber-reinforced polymer composites, *Polym. Compos.* 46 (2025) 3883–3908.
- [4] A.J. Ruys, Metal-reinforced ceramics, Woodhead Publishing, 2020.
- [5] G.I. Edo, W. Ndudi, A.B.M. Ali, E. Yousif, K. Zainulabdeen, P.N. Onyibe, P.O. Akpoghelie, H.A. Ekokotu, E.F. Isoje, U.A. Igbuku, An updated review on the modifications, recycling, polymerization, and applications of polymethyl methacrylate (PMMA), *J. Mater. Sci.* 59 (2024) 20496–20539.
- [6] M.S. Zafar, Prosthodontic applications of polymethyl methacrylate (PMMA): An update, *Polymers* (Basel). 12 (2020) 2299.
- [7] S. Shabahang, S. Kim, S. Yun, Light-guiding biomaterials for biomedical applications, *Adv. Funct. Mater.* 28 (2018) 1706635.
- [8] N.S. Radhi, N.M. Sahi, Z. Al-Khafaji, Investigation Mechanical and Biological Properties of Hybrid PMMA Composite Materials as Prosthesis Complete Denture, *Egypt. J. Chem.* (2022). <https://doi.org/10.21608/EJCHEM.2022.110545.5034>.
- [9] A.M. Díez-Pascual, PMMA-based nanocomposites for odontology applications: a state-of-the-art,

Int. J. Mol. Sci. 23 (2022) 10288.

[10] N.S. Radhi, N.E. Kareem, Z.S. Al-Khafaji, N.M. Sahig, M.W. Falah, Investigation Biological and Mechanical Characteristics of Hybrid PMMA Composite Materials as Prosthesis Complete Denture, (2022).

[11] N.S. Radhi, N.E. Kareem, Z.S. Al-Khafaji, N.M. Sahi, M.W. Falah, Investigation Biological and Mechanical Characteristics of Hybrid PMMA Composite Materials as Prosthesis Complete Denture, Egypt. J. Chem. 65 (2022) 681–688. <https://doi.org/10.21608/EJCHEM.2022.110545.5034>.

[12] T. Stern, G. Marom, Fracture Mechanisms and Toughness in Polymer Nanocomposites: A Brief Review, J. Compos. Sci. 8 (2024) 395.

[13] B. Al-Zubaidy, N.S. Radhi, Z.S. Al-Khafaji, Study the effect of thermal impact on the modelling of (titanium-titania) functionally graded materials by using finite element analysis, Int. J. Mech. Eng. Technol. (2019).

[14] S. Sattar, Y. Alaiwi, N.S. Radhi, Z. Al-khafaji, Numerical Simulation for Effect of Composite Coating (TiO₂ + SiO₂) Thickness on Steam Turbine Blades Thermal and Stress Distribution, Acad. J. Manuf. Eng. 21 (2023).

[15] H.A. Sallal, M.H. Mahboba, M.S. Radhi, A. Hanif, Z.S. Al-Khafaji, S. Ahmad, Z.M. Yaseen, Effect of adding (ZrO₂-ZnO) nanopowder on the polymer blend (lamination and methyl vinyl silicone) in a hybrid nanocomposite material, J. King Saud Univ. 36 (2024) 103061.

[16] A.A. Abd, Z. Al-khafaji, Study the Effect of Adding Malic Anhydride and Carbon Fibers to the Mechanical and Morphology Properties of Polypropylene, J. Adv. Res. Micro Nano Eng. 1 (2024) 1–10.

[17] N.S. Radhi, Z.S. Al-Khafaji, Preparation and Investigation composite coating (Ni-nano hydroxyapatite) on low carbon steel samples, in: 6th Int. Sci. Conf. Nanotechnology, Adv. Mater. Its Appl., 2018. <https://doi.org/10.13140/RG.2.2.10097.79201>.

[18] Z. Zhong, X. Jiang, H. Sun, Z. Wu, L. Yang, A. Matamoros-Veloza, Recent research on the optimization of interfacial structure and interfacial interaction mechanisms of metal matrix composites: A review, Adv. Eng. Mater. 26 (2024) 2401392.

[19] S. Lettieri, M. Pavone, A. Fioravanti, L. Santamaria Amato, P. Maddalena, Charge carrier processes and optical properties in TiO₂ and TiO₂-based heterojunction photocatalysts: A review, Materials (Basel). 14 (2021) 1645.

[20] C.-K. Lin, J.-W. Xie, P.-J. Tsai, H.-Y. Wang, Z.-W. Lu, T.-Y. Lin, C.-Y. Kuo, The Effects of Different Blending Methods on the Thermal, Mechanical, and Optical Properties of PMMA/SiO₂ Composites, J. Compos. Sci. 8 (2024) 369.

[21] Ş. Tălu, N. Patra, 3D surface characterization of polymer-oxide nanocomposite coating using nanoscale stereometric approach for enhanced functionality, Colloids Surfaces A Physicochem. Eng. Asp. 711 (2025) 136360.

[22] Z. Zhang, Z. Chen, L. Shang, Y. Zhao, Structural color materials from natural polymers, Adv. Mater. Technol. 6 (2021) 2100296.

[23] I. Mzabri, M. Addi, A. Berrichi, Traditional and modern uses of saffron (*Crocus sativus*), Cosmetics 6 (2019) 63.

[24] A.B.A. Ahmed, R.M. Taha, N. Anuar, H. Elias, S. Abdullah, A. Khan, V. Lobo, R. Vidhyavathi, Saffron

as a natural food colorant and its applications, in: Saffron, Elsevier, 2021: pp. 221–239.

[25] C.H.M. Caris, R.P.M. Kuijpers, A.M. Van Herk, A.L. German, Kinetics of (CO) polymerizations at the surface of inorganic submicron particles in emulsion-like systems, in: *Makromol. Chemie. Macromol. Symp.*, Wiley Online Library, 1990: pp. 535–548.

[26] Y. Chen, H. Xu, T. Sun, Preparation and study of PMMA/TiO₂ nanocomposites, *Adv. Mater. Res.* 233 (2011) 1830–1833.

[27] S. Agarwal, V.K. Saraswat, Synthesis and thermal characterization of PMMA-TiO₂ nanocomposites, *Mater. Sci. Res. India* 11 (2014) 168–172.

[28] S.J. Kadhem, Optical properties for TiO₂ / PMMA nanocomposite thin films prepared by plasma jet, *Iraqi J. Phys.* 15 (2018) 24–28. <https://doi.org/10.30723/ijp.v15i35.50>.

[29] N.A.H. Darweesh, M.F. Hadi, A.A. Saeed, Investigate Physical Properties and Intensity of Sun Light Transmitted through Safranin/PMMA Films, *Al-Mustansiriyah J. Sci.* 33 (2022) 86–92. <https://doi.org/10.23851/mjs.v33i2.1101>.

[30] D.A. Hameed, M.H. Shinen, A.I. Obayes, Preparation and Characterization of Structural and Biological Properties of Nano-Hydroxyapatite Composite Films with Saffron Dye Based on Polymethylmethacrylate., in: *Ann. Chim. Sci. Des Matériaux*, 2025.

[31] D.A. Hammed, M.H. Shinen, A.I. Obayes, Extracting a Plant Dye (Saffron Dye) Used as Antibiotic to Treat Bacterial Diseases, *Lett. High Energy Phys.* 2024 (2024) 524–532.

[32] M.K. Esfahani, M. Abedi, Z. Bahreini, The effect of ethanol-water mixture on ultrasonic extraction of crocin from saffron, *Saffron Agron. Technol.* 9 (2021) 285–293.

[33] J.E. ten Elshof, Chemical solution deposition techniques for epitaxial growth of complex oxides, in: *Ep. Growth Complex Met. Oxides*, Elsevier, 2015: pp. 69–93.

[34] J. Ouyang, H. Huang, X. Chen, J. Chen, Biodegradable Polymer/TiO₂ Nanotubes Loaded Roxithromycin as Nanoarray Capsules for Long-Lasting Antibacterial Properties of Titanium Implant, *J. Nanomater.* 2020 (2020) 5432926.

[35] D.A.H. Hanaor, C.C. Sorrell, Review of the anatase to rutile phase transformation, *J. Mater. Sci.* 46 (2011) 855–874.

[36] P. Makuła, M. Pacia, W. Macyk, How to correctly determine the band gap energy of modified semiconductor photocatalysts based on UV–Vis spectra, *J. Phys. Chem. Lett.* 9 (2018) 6814–6817.

[37] E. Akdogan, M. Erdem, M.E. Ureyen, M. Kaya, Synergistic effects of expandable graphite and ammonium pentaborate octahydrate on the flame-retardant, thermal insulation, and mechanical properties of rigid polyurethane foam, *Polym. Compos.* 41 (2020) 1749–1762.

[38] S. Chang, Analysis of polymer standards by Fourier transform infrared spectroscopy-attenuated total reflectance and pyrolysis gas chromatography/mass spectroscopy and the creation of searchable libraries, *Forensic Sci. Intersh. Marshall Univ. Forensic Sci. Progr.* (2012) 1–46.

[39] Z. Vuluga, M.C. Corobeia, C. Elizetxea, M. Ordóñez, M. Ghiurea, V. Raditoiu, C.A. Nicolae, D. Florea, M. Iorga, R. Somoghi, Morphological and tribological properties of PMMA/halloysite nanocomposites, *Polymers (Basel).* 10 (2018) 816.

[40] M. Alamgir, A. Mallick, G.C. Nayak, S.K. Tiwari, Development of PMMA/TiO₂ nanocomposites as excellent dental materials, *J. Mech. Sci. Technol.* 33 (2019) 4755–4760.

[41] N. Chand, N. Siddiqui, Improvement in thermo mechanical and optical properties of in situ

synthesized PMMA/TiO₂ nanocomposite, *Compos. Interfaces* 19 (2012) 51–58.

[42] X. Chen, S.S. Mao, Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications, *Chem. Rev.* 107 (2007) 2891–2959.

[43] B. Banerjee, V. Amoli, A. Maurya, A.K. Sinha, A. Bhaumik, Green synthesis of Pt-doped TiO₂ nanocrystals with exposed (001) facets and mesoscopic void space for photo-splitting of water under solar irradiation, *Nanoscale* 7 (2015) 10504–10512.

[44] A. Kausar, P. Bocchetta, Poly (methyl methacrylate) nanocomposite foams reinforced with carbon and inorganic nanoparticles—state-of-the-art, *J. Compos. Sci.* 6 (2022) 129.

[45] M.S. Kavşut, Tuning Optical and Dielectric Properties of Phpma/Tio₂ Nanocomposites: Effect of Direct Mixing vs. Surface Grafting, (n.d.).

[46] H. Xu, Z. Hao, C. Wang, J. Deng, T. Wang, J. Zhang, In situ emulsion polymerization to multifunctional polymer nanocomposites: a review, *Macromol. Chem. Phys.* 224 (2023) 2300185.

[47] A. Razaghizadeh, V. Rafee, R. Nakhaei, Effect of silver nanoparticles embedding in mesoporous TiO₂ layer on the performance enhancement of dye-sensitized solar cells using natural dyes, *Plasmonics* (2025) 1–15.

الخلاصة

يُقدم هذا العمل لأول مرة تطوير وتحسين وتصنيف البنية لمتراتب نانوي من بولي (ميثيل ميثاكريلات) (PMMA) المدعّم بجزيئات نانوية من ثاني أكسيد التيتانيوم (TiO_2) والمفعّل بصبغة الزعفران الطبيعية المستخلصة من نبات *Crocus sativus* L.. يهدف هذا البحث إلى إنشاء فئة جديدة من المواد الهجينة المستدامة ذات الخصائص المتعددة المحسّنة.

تم تحضير هذه المتراتبات باستخدام طريقي الصبّ من المحلول (solution casting) والطلاء بالغمس (dip-coating) مع نسب مختلفة من TiO_2 (0.2، 0.4، 0.6 وزن%)، وتم التركيز بشكل خاص على تأثيرها في البنية المورفولوجية والتوزيع والتفاعلات البنية.

تم إجراء التحليل البنائي والكيميائي والبلوري للمتراتبات باستخدام تقنيات حيود الأشعة السينية (XRD) ، والأشعة تحت الحمراء بتحويل فوريه ATR-FTIR ، والمجهر الإلكتروني الماسح عالي الدقة (FESEM) مع تحليل الصور باستخدام برنامج ImageJ لتحديد درجة تشتت الجسيمات النانوية.

أظهرت النتائج وجود طور الأناتاز البلوري لثاني أكسيد التيتانيوم، وطور PMMA غير المتببور، مع وجود ترابط واجهي جيد بين المكونات تسهّله صبغة الزعفران، بالإضافة إلى توزيع متباين مع ظهور تجمعات بسيطة عند نسب التحميل العالية. وتشير النتائج إلى وجود تفاعل واجهي قوي بين المكونات. كما أظهرت الجسيمات انخفاضاً ملحوظاً في الحجم من نحو 45 نانومتراً عند أقل نسبة TiO_2 إلى 10 نانومترات، مما يدل على تأثير الصبغة في تحسين التشتت الطبيعي.

ساهمت إضافة TiO_2 في تعزيز التماسك والبنية، بينما أضفت صبغة الزعفران وظائف بصرية وبيولوجية على هذا النظام المتراتب النانوي الجديد، مما يجعله واعداً لتطبيقات محتملة في المواد البصرية الإلكترونية، والطلاءات الطبية الحيوية، وتطوير المواد الصديقة للبيئة.

الكلمات المفتاحية: المواد المركبة، بولي (ميثيل ميثاكريلات) (PMMA)، صبغة الزعفران الطبيعية (*Crocus sativus* L.).، الجسيمات النانوية لثاني أكسيد التيتانيوم (TiO_2).